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(54) THERMOSENSITIVE RECORDING ELEMENT HAVING IMPROVED SMOOTHNESS CHARACTERISTICS

WARMEEMPFLINDLICHES AUFZEICHNUNGSMATERIAL MIT VERBESSERTEN
GLATTHEITSKARAKTERISTIK

ELEMENT D'ENREGISTREMENT THERMOSENSIBLE AYANT DES CARACTERISTIQUES
AMELIOREES D'EGALITE DE SURFACE

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- TAPPI JOURNAL, Volume 71, No. 7, July 1988, A.S. Campbell et al, "Bond paper characteristics for printing by resistive ribbon thermal transfer" page 140 - page 144; see esp. page 143, column 2 - column 3
- TAPPI, Volume 63, No. 11, November 1980, Keith E. Bradway, "Comparison of smoothness evaluated by different test methods", page 95 - page 98; see esp. page 97, column 1 - page 98, column 1

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DescriptionFIELD OF THE INVENTION

5 This invention relates to thermosensitive recording elements and, in particular, to thermosensitive recording elements having improved smoothness. Further this invention relates to a process for preparing thermosensitive recording elements having improved smoothness.

BACKGROUND OF THE INVENTION

10 Thermosensitive recording elements have wide application in the printing industry. For example, thermosensitive recording elements have been used in recording instruments for measurements such as facsimiles, printers, thermal devices for computers, devices for preparing architectural and engineering drawings, automatic vending machines for dispensing railroad tickets and luggage tags, and thermal label printing devices. Conventional thermosensitive recording
 15 elements generally comprise a support and a thermosensitive recording layer provided thereon. The thermosensitive recording layer primarily contains a binder, a substantially colorless electron donating dye precursor and an electron accepting compound, also known as a developer. Heat is applied to the element by means of a thermal head, a thermal pen or laser beam, and upon heating, the dye precursor instantaneously reacts with the electron accepting compound to form a recorded image.

20 Thermosensitive recording elements are typically prepared by finely dispersing the electron donating dye precursor and the electron accepting compound in an aqueous solution of a water soluble binder. For example, U.S.-A-4,717,593, issued to Igarashi et al. on January 5, 1988, describes a heat sensitive recording sheet obtained by applying aqueous dispersions of an electron donating colorless dye and an electron accepting compound to a base. At least one of the aqueous dispersion of the electron donating colorless dye and the aqueous dispersion of the electron accepting com-
 25 pound is prepared by dispersing by means of a horizontal sand mill to obtain an average particle size of about .5 to 3 μm . Dispersions prepared in this manner are coated onto a support such as paper and the coated paper is then dried. The imaging surface of thermosensitive recording elements prepared in this manner is not very smooth. This surface irregularity causes less than optimum contact of the element with the print head of thermal recorders. Thus, non-uniform images are formed. It has been found that passing the finished thermosensitive recording element through a calender
 30 produces a smooth coated surface which provides optimum contact with the print head of thermal recorders. However, post coating calendering is disadvantageous in that (1) it requires expensive equipment and (2) it may decrease yields of the finished element and thus cause an increase in manufacturing costs.

35 Accordingly, a need exists for a thermosensitive recording element having improved smoothness without the disadvantages associated with conventional post coating calendering. It has been found that the thermosensitive elements of the invention overcomes these disadvantages.

SUMMARY OF THE INVENTION

The present invention provides a thermosensitive recording element comprising:

- 40 (a) a support having a Sheffield smoothness of less than 60; and
 (b) at least one layer in contact with the support, said layer comprising an organic polymeric binder, a substantially colorless electron donating dye precursor and an electron accepting compound capable of forming color by reacting with said dye precursor, wherein the dye precursor and the electron accepting compound have a particle size of
 45 less than 3 μm .

In a preferred embodiment of the invention, the thermosensitive recording element comprises:

- 50 (a) a support having a Sheffield smoothness of less than 60;
 (b) a first layer comprising an organic polymeric binder and a substantially colorless electron donating dye precursor; and
 (c) a second layer comprising an organic polymeric binder compatible with the binder in (b), an electron accepting compound capable of forming color by reaction with said dye precursor, and a crosslinking agent, wherein the first layer is interposed between the support and the second layer, and wherein the dye precursor and the electron
 55 accepting compound have a particle size of less than 3 μm .

In another preferred embodiment of the invention, the thermosensitive recording element comprises:

- (a) a support having a Sheffield smoothness of less than 60;

(b) a first layer comprising an organic polymeric binder and either a substantially colorless electron donating dye precursor, an electron accepting compound, or mixtures thereof; and

(c) a second layer comprising an organic polymeric binder compatible with the binder in (b) and either a substantially colorless electron donating dye precursor or an electron accepting compound, wherein both dye precursor and electron accepting compound are present in the element, wherein the dye precursor and electron accepting compound have a particle size of less than 3 μm and wherein the first layer is interposed between the support and second layer.

Other embodiments of the invention include processes for preparing these thermosensitive recording elements.

DETAILED DESCRIPTION OF THE INVENTION

Surprisingly and unexpectedly, it was found that the use of a support having a Sheffield smoothness less than 60 with a thermosensitive layer applied thereon wherein the layer comprises a dye precursor and an electron accepting compound having a particle size less than 3 μm produced an element having improved surface smoothness. Thus, compared to conventional thermosensitive recording elements, these thermosensitive elements did not have to be calendered to obtain a smooth surface.

The thermosensitive recording element of the invention comprises a support, and a layer in contact with the support comprising an organic polymeric binder, a substantially colorless electron donating dye precursor and an electron accepting compound, wherein the support has a Sheffield smoothness of less than 60, preferably 15-25, and the dye precursor and the electron accepting compound have a particle size of less than 3 μm , preferably 0.8-1 μm .

In one preferred embodiment, the thermosensitive recording element of the invention comprises a support; a first layer comprising an organic polymeric binder and a substantially colorless electron donating dye precursor; and a second layer comprising an organic polymeric binder compatible with the binder in (b), an electron accepting compound capable of forming color by reaction with said dye precursor, and a crosslinking agent, wherein the first layer is interposed between the support and the second layer, and wherein the support has a Sheffield smoothness of less than 60, and the dye precursor and electron accepting compound have a particle size of less than 3 μm .

In another preferred embodiment, the thermosensitive recording element of the invention comprises a support; a first layer comprising an organic polymeric binder and either a substantially colorless electron donating dye precursor, an electron accepting compound, or mixtures thereof; and a second layer comprising an organic polymeric binder compatible with the binder in (b) and either a substantially colorless electron donating dye precursor or an electron accepting compound, wherein the first layer is interposed between the support and second layer and both dye precursor and electron accepting compound are present in the element, and wherein the support has a Sheffield smoothness of less than 60, and the dye precursor and electron accepting compounds have a particle size of less than, 3 μm .

SUPPORTS

The thermosensitive elements of the invention must contain a support having a Sheffield smoothness of less than 60 and preferably 15-25, to produce an element having improved smoothness. Sheffield smoothness is determined using the method described in TAPPI Test Methods, T 538 om-88, Vol. 1, 1991. Suitable supports include sheet-formed materials such as paper, e.g., 100% bleached Kraft composed of a blend of hard and soft wood, 100% wood free cotton vellum, and wood-containing paper made translucent either by pulp beating or with additives.

Supports may be provided with a sealant layer comprising an inorganic pigment, preferably a blend of inorganic pigments, and a latex sealant. The presence of the sealant layer allows for the reduction in coating weight of the layer or layers containing the dye precursor and the electron accepting compound without sacrificing image density. Some useful pigments include kaolin clay, e.g., calcined kaolin clay; calcium carbonate; titanium dioxide; barium sulfate, talc; etc. A preferred blend of pigments includes kaolin clay (70-80%), calcium carbonate (15-20%), and, titanium dioxide (5-20%). Preferably the ratio of the pigments in the blend is 70:15:5%. Some useful latex sealants include acrylic resins, styrene-butadiene type resins, acetates, natural binders such as starches, and blends thereof. The latex preferred sealant is a styrene/butadiene resin having a Tg of 3°C, and a minimum film forming temperature of + 5°C. The amount of latex sealant is 18-24% based on the total pigment weight, preferably 19-22%.

ELECTRON DONATING DYE PRECURSOR

The thermosensitive recording element of the invention contain a substantially colorless electron donating dye precursor. By the term "substantially colorless" it is meant having a background optical density less than or equal to 0.10.

Electron donating dye precursors used in ordinary pressure-sensitive recording papers, thermosensitive recording papers, etc., are useful in the present invention. Suitable electron donating dye precursors are disclosed in U.S.-A-

4,889,841 issued to Kosaka et al., 4,885,271 issued to Kawakami et al., and 4,467,336 issued to Koike. Specific examples include:

- (1) triarylmethane compounds such as 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide (Crystal Violet lactone), 3,3-bis(p-dimethylaminophenyl)-phthalide, 3-(p-dimethylaminophenyl)-3-(1,2-dimethylindol-3-yl)phthalide, 3-(p-dimethylaminophenyl)-3-(2-methylindol-3-yl)phthalide, 3-(p-dimethylamino-phenyl)-3-(2-phenylindol-3-yl)phthalide, 3,3-bis(1,2-dimethyl-indol-3-yl)-5-dimethylaminophthalide, 3,3-bis(1,2-dimethylindol-3-yl)-6-dimethylaminophthalide, 3,3-bis(9-ethylcarbazol-3-yl)-5-dimethylaminophthalide, 3,3-bis(2-phenylindol-3-yl)-5-dimethylaminophthalide, 3-p-dimethylaminophenyl-3-(1-methylpyrrol-2-yl)-6-dimethylaminophthalide;
- (2) diphenylmethane compounds such as 4,4'-bis-dimethylaminobenzhydryl benzyl ether, N-halophenyl leuco Auramine, N-2,4,5-trichlorophenyl leuco Auramine;
- (3) xanthene compounds such as Rhodamine B anilinolactam, Rhodamine B p-chloroanilinolactam, 3-diethylamino-7-dibenzylaminofluoran, 3-diethylamino-7-octylaminofluoran, 3-diethylamino-7-(3,4-dichloroanilino)fluoran, 3-diethylamino-7-(2-chloroanilino)fluoran, 3-diethylamino-6-methyl-7-anilinofluoran, 3-piperidino-6-methyl-7-anilinofluoran, 3-ethyltolylamino-6-methyl-7-anilinofluoran, 3-ethyltolylamino-6-methyl-7-phenylfluoran, 3-diethylamino-7-(4-nitroanilino)fluoran, 3-dibutylamino-6-methyl-7-anilinofluoran, 3-(N-methyl-N-propyl)amino-6-methyl-7-anilinofluoran, 3-(N-ethyl-N-isopropyl)amino-6-methyl-7-anilinofluoran, 3-(N-ethyl-N-tetrahydrofurfuryl)amino-6-methyl-7-anilinofluoran, 3-(N-ethyl-N-isopentyl)amino-6-methyl-7-anilinofluoran; 3-(N-cyclohexyl-N-methyl)amino-6-methyl-7-anilinofluoran; 3-diethylamino-6-methyl-7-anilinofluoran; 3-dibutylamino-6-methyl-7-anilinofluoran; 3-(N-ethyl-N-(3-ethoxy)propyl)amino-6-methyl-7-anilinofluoran; 3-dipentyl-amino-6-methyl-7-anilinofluoran;
- (4) thiazine compounds such as benzoyl leuco methylene blue, p-nitrobenzoyl leuco methylene blue; and
- (5) spiro compounds such as 3-methyl-spirodinaphthopyran, 3-ethyl-spirodinaphthopyran, 3,3'-dichlorospirodinaphthopyran, 3-benzyl-spirodinaphthopyran, 3-methylnaphtho-(3-methoxybenzo)spiropyran, 3-propyl-spirodibenzo-pyran. Also useful are mixtures of these dye precursors.

Preferred electron donating dye precursors suitable for practicing the invention are (i) 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide, (ii) 3-(N-ethyl-N-isopentyl)-amino-6-methyl-7-anilinofluoran and (iii) 3-dipentylamino-6-methyl-7-anilinofluoran. The electron donating dye precursor can be used in the amount of 1 to 15%, preferably 3 to 8%, by weight based on the weight of the coating composition.

ELECTRON ACCEPTING COMPOUND

The thermosensitive elements of the invention also comprise an electron accepting compound. Suitable electron accepting compounds, also known as acidic developers, are disclosed in U.S.-A-4,889,841 issued to Kasaka et al., 4,885,271 issued to Kawakami et al., and 4,467,336 issued to Koike. Some specific types of electron accepting compounds include phenol derivatives, aromatic carboxylic acid derivatives, N,N'-diarylthiourea derivatives, and polyvalent metal salts such as zinc salts of organic compounds.

Particularly preferred electron accepting compounds are phenol derivatives. Specific examples include p-octylphenol, p-tert-butylphenol, p-phenylphenol, 1,1-bis(p-hydroxyphenyl)propane, 1,1-bis(p-hydroxyphenyl)pentane, 1,1-bis(p-hydroxyphenyl)hexane, 2,2-bis(p-hydroxyphenyl)hexane, 1,1-bis(p-hydroxyphenyl)-2-ethylhexane, 2,2-bis(4'-hydroxyphenyl)propane, 2,2-bis(4-hydroxy-3-dichlorophenyl)propane, benzyl p-hydroxybenzoate, ethyl p-hydroxybenzoate, butyl p-hydroxybenzoate, p-p'-dihydroxydiphenylsulfone, 2,2'-diallyl-4,4'-dihydroxydiphenylsulfone, and 2,2'-dimethyl-4,4'-dihydroxydiphenylsulfide. Mixtures of these compounds may also be used.

The electron accepting compounds can be used in the amount of 50 to 500%, preferably 100 to 200%, by weight based on the weight of the dye precursor.

BINDERS

Binders useful for practicing the invention are water soluble binders having a molecular weight of 20,000 to 200,000 such as starches, hydroxyethyl cellulose, methyl cellulose, carboxymethyl cellulose, soluble collagen, gelatin, casein, polyacrylamide, polyvinyl pyrrolidone, polyvinyl alcohol, polyvinyl alcohol copolymers such as poly(vinyl alcohol-co-vinyl acetate) also known as partially hydrolyzed polyvinyl alcohol, sodium alginate, water soluble phenol formaldehyde resins, styrene-maleic anhydride copolymer, ethylene-maleic anhydride copolymer, ethylene vinyl acetate polymers; latex type water soluble binders such as styrene-butadiene copolymer, acrylonitrile-butadiene copolymer, methyl acrylate-butadiene copolymer, etc., acrylic resins such as poly(methyl methacrylate/ethyl acrylate/acrylic acid).

The organic polymeric binder is present as an aqueous solution having a concentration of 1 to 20% by weight, preferably 3 to 10% by weight. If the concentration is less than 1%, stability of the dispersed particles will be inferior and cohesion may occur during the heating step. If the concentration is greater than 20%, the viscosity of the dispersion increases remarkably thus requiring a large amount of energy to perform the dispersion.

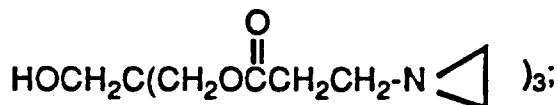
In the preferred embodiments, where two layers are formed on top of the support, it is important that the binder in the second layer be compatible with the binder in the first layer. By the term "compatible with the binder," it is meant that the binder in the second layer is either identical to or has similar properties to the binder in the first layer. For example, it is important that the two binders are miscible with one another and that they do not chemically react with one another.

CROSSLINKING AGENTS

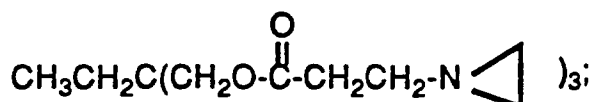
In one preferred embodiment of the invention, the second layer of the thermosensitive element contains a crosslinking agent. It is believed that the crosslinking agent forms crosslinked acetal linkages with the pendant hydroxyl groups in the polymeric binder. Crosslinking agents useful in practicing the invention are those which are known to crosslink organic polymeric binders, such as mono and polyfunctional aldehydes, e.g., formaldehyde and free dialdehydes, such as glyoxal, succinaldehyde and glutaraldehyde, as described in U.S.-A-3,232,764 issued to Allen et al.; and blocked dialdehydes, as described by Kaszuba, U.S. Patent No. 2,586,168, Jeffreys, U.S.-A-2,870,013, and Yamamoto et al., U.S.-A-3,819,608;

Other useful crosslinking agents include (a) α -diketones, as described by Allen et al. in U.S.-A-2,725,305; (b) active esters of the type described by Burness et al., in U.S.-A-3,542,558; (c) active halogen compounds as described by Burness in U.S.-A-3,106,468; Silverman et al., U.S.-A-3,839,042, Ballantine et al., U.S.-A-3,951,940; and Himmelmann et al., U.S.-A-3,174,861; (d) s-triazines and diazines, as described by Yamamoto et al., U.S.-A-3,325,287; Anderau et al., U.S.-A-3,288,775; and Stauner et al., U.S.-A-3,992,366; (e) epoxides, as described by Allen et al., U.S.-A-3,047,394; Burness, U.S.-A-3,189,459; and Birr et al., DE-A-1,085,663; (f) aziridines, as described by Allen et al., U.S.-A-2,950,197; Burness et al., U.S.-A-3,271,175; and Sato et al., U.S.-A-3,575,705.

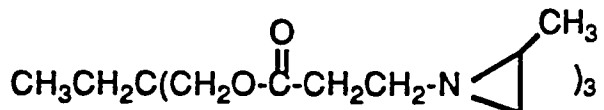
Crosslinking agents of mixed function, such as halogen-substituted aldehyde acids, e.g., mucochloric and mucobromic acids, as described by White, U.S.-A-2,080,019 may also be used in practicing the invention. In addition, vinyl sulfones containing other hardening functional groups, as described by Sera et al., U.S.-A-4,028,320; and polymeric crosslinking agents, such as dialdehyde starches, as described by Jeffreys et al., U.S.-A-3,057,723; and copoly(acrolein-methacrylic acid), as described by Himmelmann et al., U.S.-A-3,396,029 can also be used as crosslinking agents. Some useful polyfunctional aziridines include: Pentaerythritol-tri[β -(N-aziridiny)propionate]:



Trimethylolpropane-tri[β -(N-aziridiny)propionate]:



and trimethylolpropane-tri[β -(N-(methylaziridiny)) propionate]



Other polyfunctional aziridines can be employed, e.g., pentaerythritol-tri[β -(N-(alkyl or dialkyl-substituted aziridiny))propionate] wherein alkyl is of 1 to 6, preferably 1 to 4, carbon atoms.

Preferred crosslinking agents used in practicing the invention are glyoxal, glutaric dialdehyde, and propionaldehyde. The crosslinking agent is present in the amount of 2 to 6% based on the total layer composition, preferably 3 to 5%.

CATALYST

Catalysts may be used in combination with the crosslinking agent. Suitable catalysts are selected from the group consisting of mineral acids, e.g., hydrochloric, hydrobromic, sulfuric, nitric, phosphoric and boric acids; organic acids, e.g., p-toluenesulfonic, p-dodecylbenzene sulfonic, trichloroacetic, trifluoroacetic, perfluoroheptanoic, acetic, etc.; and

an acid from a compound supplying acid, e.g., Lewis acid selected from the group consisting of zinc chloride, zinc bromide, ferric chloride. The preferred catalyst in practicing the invention is p-toluenesulfonic acid. The catalyst is present in the amount of 0.3 to 2% based on the total layer composition, preferably 0.4 to 1%.

5 ADDITIVES

Additives may be present in the dye precursor-containing layer and the developer-containing layer. Additives suitable for practicing the invention include pigments, waxes, lubricants, activation cosolvents, higher fatty acid metal salts, surface active agents, mold inhibitors, dispersing agents, UV absorbing agents, fluorescent dyes, optical brighteners, defoaming agents, and the like. Also useful are heat fusible materials which may lower the melting point of the dye precursor or developer to improve color sensitivity at low temperatures. Preferably, the waxes and higher fatty acid metal salts are in the uppermost layer where they assist in preventing the thermosensitive element from sticking to or scratching the thermal head of the recording device.

Useful pigments include diatomaceous earth, talc, kaolin, sintered kaolin, calcium carbonate, magnesium carbonate, titanium oxide, zinc oxide, silicon oxide, aluminum hydroxide, urea-formalin resin.

Useful heat fusible materials include B-naphthol benzylether, p-benzylbiphenyl, ethylene glycol m-tolyl ether, m-terphenyl, bis(2-(4-methoxy)phenoxyethyl)ether, dibenzyl oxalate, di(p-chlorobenzyl)oxalate, di(p-methylbenzyl)oxalate and dibenzyl terephthalate. These heat fusible materials may be used in the amount of 25-500%, preferably 50 to 200%, by weight based on the weight of dye precursor.

Examples of higher fatty acid metal salts are zinc stearate, calcium stearate. Useful waxes include paraffin, oxidized paraffin, polyethylene, oxidized polyethylene, stearic amide and castor wax. Dispersing agents such as sodium dioctyl-sulfosuccinate; UV absorbing agents of the benzophenone type, benzotriazole type; and mold inhibitors such as sodium-o-phenylphenate tetrahydrate, are also useful additives.

25 DISPERSION PREPARATION AND COATING

Another process is provided for preparing a thermosensitive recording element comprising a support having a Sheffield smoothness of less than 60, and at least one layer provided thereon wherein said layer comprises a binder, a substantially colorless electron donating dye precursor and an electron accepting compound capable of forming color by reacting with said dye precursor wherein the dye precursor and electron accepting compound have a particle size of less than 3 μm . The process for making such an element comprises the steps of:

- (a) providing a support;
- (b) preparing a first dispersion of an aqueous solution comprising an organic polymeric binder and a substantially colorless, electron donating dye precursor;
- (c) preparing a second dispersion of an aqueous solution comprising an organic polymeric binder, an electron accepting compound capable of forming color by reaction with said dye precursor, wherein the binder is compatible with the binder in (b);
- (d) preparing a mixture of the first and second dispersions;
- (e) applying the mixture of the first and second dispersions onto the support; and
- (f) drying the dispersion applied in step (e) to form a first layer on the support, wherein the support has a Sheffield smoothness of less than 60, and the dye precursor and electron accepting compound have a particle size of less than 3 μm .

Dispersions of the dye precursor and electron accepting compound are generally prepared with an aqueous solution of the organic polymeric binder as the dispersion medium.

The dispersion containing the dye precursor is prepared by grinding the dye precursor and optionally other suitable additives along with an aqueous solution of the organic polymeric binder in a grinding device such as a ball mill; sand mill such as a horizontal sand mill; an attritor, etc. Preferably a horizontal sand mill containing zirconium silicate media is used. The dispersion is subjected to continuous grinding until an average particle size of 0.5-3 μm , preferably 0.8-1 μm is obtained.

The electron accepting compound containing dispersion is prepared by grinding the electron accepting compound, aqueous solution of the organic polymeric binder and suitable additives in one of the above described grinding devices until an average particle size of 0.5-3 μm , preferably 0.8-1 μm , is obtained.

The dye precursor and the electron accepting compound in their respective dispersions have a particles size of about 0.5-3 μm , preferably 0.8-1 μm . Thermal response in the thermosensitive element is generally insufficient if the particle size is greater than 3 μm . A particle size less than 0.5 μm can either result in fogging or require a significant amount of energy to carry out the dispersion.

The dye precursor containing dispersion and the dispersion containing the electron accepting compound are mixed and applied to the support. The applied dispersion is then dried thereby forming a first layer on the support. The ratio of the dye precursor to the electron accepting compound in this layer is in the range of 1:1 to 10:1, preferably 2:1 to 4:1.

Alternatively, separate dispersions containing either the dye precursor, or the electron accepting compound, may be prepared by grinding the dye precursor or electron accepting compound with an aqueous solution of the organic polymeric binder in a grinding device until the desired average particle size is reached. In preparing the respective dispersions, suitable additives as well as a catalyst may be added. A suitable crosslinking agent is added to the dispersion containing the electron accepting compound. Coating dispersions or compositions may then be prepared by blending the individual dispersions in ratios that produce the desired weight percentage of the individual ingredients as a percentage of total weight of the coating dispersion.

Accordingly, the invention provides a process for preparing a thermosensitive recording element comprising (a) a support having a Sheffield smoothness of less than 60, (b) a first layer comprising an organic polymeric binder and a substantially colorless electron donating dye precursor, and (c) a second layer comprising an organic polymeric binder compatible with the binder in (b), an electron accepting compound capable of forming color by reaction with said dye precursor, and a crosslinking agent, wherein the first layer is interposed between the support and the second layer, and wherein the dye precursor and the electron accepting compound have a particle size of less than 3 μm .

The process for making such an element comprises the steps of

- (a) providing a support;
- (b) preparing a first dispersion of an aqueous solution comprising an organic polymeric binder and a substantially colorless, electron donating dye precursor;
- (c) preparing a second dispersion of an aqueous solution comprising an organic polymeric binder compatible with the binder in (b), an electron accepting compound capable of forming color by reaction with said dye precursor, and a crosslinking agent;
- (d) applying the first dispersion onto the support;
- (e) drying the applied first dispersion to form a first layer on the support;
- (f) applying the second dispersion on the first layer formed in step (e); and
- (g) drying the second applied dispersion to form a second layer, wherein the support has a Sheffield smoothness of less than 60, and the dye precursor and electron accepting compound have a particle size of less than 3 μm .

Another process for preparing a thermosensitive recording element comprising (a) a support having a Sheffield smoothness of less than 60, (b) a first layer comprising an organic polymeric binder and either a substantially colorless electron donating dye precursor, an electron accepting compound, or mixtures thereof, (c) a second layer comprising an organic polymeric binder compatible with the binder in (b) and either a substantially colorless electron donating dye precursor or an electron accepting compound, wherein both dye precursor and electron accepting compound are present in the element, wherein the dye precursor and electron accepting compound have a particle size of less than 3 μm and wherein the first layer is interposed between the support and second layer. The process for making such an element comprises the steps of:

- (a) providing a support;
- (b) preparing a first dispersion of an aqueous solution of an organic polymeric binder containing a substantially colorless, electron donating dye precursor;
- (c) preparing a second dispersion of an aqueous solution of an organic polymeric binder containing an electron accepting compound, wherein the binder is compatible with the binder in (b);
- (d) applying either the first dispersion, the second dispersion or a mixture thereof onto the support;
- (e) drying the first applied dispersion to form a first layer on the support;
- (f) applying either the first dispersion or the second dispersion on the first layer formed in step (e); and
- (g) drying the dispersion applied in step (f) to form a thermosensitive recording element having a support bearing at least two layers, wherein the support has a Sheffield smoothness of less than 60, and the dye precursor and electron accepting compound have a particle size of less than 3 μm .

In each of the above-described processes, the dispersions comprising dye precursor and electron accepting compound are mixed using conventional mixing devices known to one skilled in the art and the dispersion mixture is applied, preferably coated, using any conventional coating apparatus, onto a support, preferably paper, followed by drying at 25°, to 50°C, preferably 45° to 50°C for 2 to 30 minutes, and more preferably 2 to 5 minutes. The dye precursor in the coated layer is present in the amount of 0.3 g/m² to 1.6 g/m², preferably 0.4 g/m² to 0.8 g/m². The electron accepting compound in the coated layer is present in the amount of 0.2 g/m² to 2.7 g/m², preferably 0.7 g/m² to 1.3 g/m². Alternatively, the electron accepting compound is present in an amount equal to 50-100%, preferably 100-200% by weight based on the weight of dye precursor present in the layer. After drying, additional layers may be applied, preferably coated onto the

dried first layer followed by drying under the same conditions. It is preferred that drying be conducted in such a fashion that the moisture content of the thermosensitive recording element is within the range of from 5% by weight to 9% by weight based on the total weight of the recording element.

Additional layers may be applied to the dried recording element thus described to impart different surface characteristics such as gloss, smoothness, color, resistance to inorganic or organic solvents, or additional abrasion resistance. In an element having more than two layers, it is preferred that the outermost layer of the recording element be free of dye precursor. It has been found that the presence of both dye precursor and electron accepting compound in the outermost layer causes the element to become too heat sensitive which can lead to "image bleeding" or "smearing" from the trailing edge of images. The additional layer or layers may comprise an organic polymeric binder compatible with the binder in the adjacent layer and a dye precursor or an electron accepting compound. It is preferred that the two outermost layers comprise either dye precursor or electron accepting compound. If a crosslinking agent and optionally a catalyst are present in the outermost layer, then the layer should not contain dye precursor or the thermosensitive element will not have improved abrasion resistance. The outermost layer may also contain compounds selected from the group consisting of pigments, waxes, higher fatty acid metal salts, optical brighteners, and mixtures thereof. The cumulative amount of electron accepting compound in all layers of the composition should fall in the range of 50-500%, preferably 100-200% by weight based on the total amount of dye precursor used in the coated material.

EXAMPLES

The following examples further illustrate, but do not limit, the invention. The parts and percentages are by weight unless otherwise noted. Average particle size was measured using a Microtrac Model 7998 SPA Particle Size Analyzer, Leeds & Northrup Co., St. Petersburg, FL.

EXAMPLE 1

The following ingredients were ground together in a 1.5 liter horizontal grinding mill containing Zirconium Silicate grinding media of 0.6-1.0 μm particle size. The dispersions were subjected to continuous grinding in the mill at residence times to 10 minutes/liter of dispersion. Analysis of the resulting dispersions showed they each contained particles with average size of 1-2 μm in diameter:

Dispersion "A" (Dye precursor Dispersion):

INGREDIENT	WEIGHT %
3-(N-diethyl)-amino-6-methyl-7-anilino-fluoran	6.4
Parabenzylbiphenyl	6.4
Polyvinylalcohol (7% in water)	87.2

Dispersion "B" (Electron accepting compound or Developer Dispersion):

INGREDIENT	WEIGHT %
p-Hydroxybenzylbenzoate	6.0
1,1,3-Tris(2-methyl-4-hydroxy-5-cyclohexylphenyl)butane	1.1
Calcium carbonate	14.9
Polyvinylalcohol (7% in water)	78.0

Base Paper

The base paper used was 100% bleached Kraft composed of a blend of hard and soft woods and was emulsion sized with synthetic cationic sizing materials. The paper was machine glazed on one surface with a Yankee dryer and then further smoothed by applying an 8.1 g/m² sealant layer containing inorganic pigments in a styrene-butadiene latex to the machine glazed surface. The inorganic pigments consisted of a blend of kaolin clay (70-80%), calcium carbonate (15-20%), and titanium dioxide (5-20%) and the latex sealant was a styrene/butadiene resin having a T_g of 3°C, and a

minimum film forming temperature of + 5°C. The resulting sheet had a smoothness of 17-20 Sheffield units as measured according to TAPPI Testing Method T538 om-88, Vol. 1, 1991 and a total base weight of 81.4 g/m².

Dispersion "A" was then applied to the above described base paper using a Meyer Rod. The coating was dried in an oven to 140°F (60°C) until its moisture content was reduced to 6-8% by weight. The coating was white in color and was shown to have a coating weight of, 1.63-2.44 g/m².

Dispersion "B" was then applied to the base paper containing coating from Dispersion "A" using a Meyer Rod. The coated paper was dried in an air oven to 130-140°F (54-60°C) until its moisture content was shown to be in the range of 6-8% by weight. The total coating thus applied to the base paper was shown to have a coating weight of 3.26-4.88 g/m². The coated paper was white in color, had low gloss as indicated by a 5-10% total reflection, and was resistant to scratching by fingernail abrasion. The coated paper was shown to have a smoothness of 17-22 Sheffield units on the coated side. It had a background absorbance of 0.02-0.05 O.D. units, as measured by reflectance densitometry, and produced a black image with a thermal printer with an absorbance of 1.20 O.D. units.

EXAMPLE 2

A dispersion of p-hydroxybenzylbenzoate (15% by weight) and 7% aqueous polyvinylalcohol (85% by weight) was prepared by grinding these ingredients in a horizontal grinding mill until the average particle size was shown to be 0.8-1.0 µm in diameter. The dispersion was blended with dye dispersion "A" from Example 1 in proportions such that the final weight percentage of the resulting Dispersion "C" was as follows:

Dispersion "C"

INGREDIENT	WEIGHT %
3-(N-diethyl)-amino-6-methyl-7-anilino-fluoran	4.8
Parabenzylobiphenyl	4.8
p-Hydroxybenzylbenzoate	2.0
Polyvinylalcohol (7% in water)	88.4

Dispersion "C" was used to coat machine glazed base paper as described in Example 1 using a Meyer Rod and dried as described in Example 1. The resulting white coating was shown to have a coating weight of 1.8-2.8 g/m². The coated paper had a smoothness of 45 Sheffield units. The coating marked easily if rubbed with a fingernail.

EXAMPLE 3

Dispersion "B" from Example 1 was applied as a top coat over the paper thus coated with Dispersion "C" from Example 2, using a Meyer Rod and dried according to the procedure described in Example 1. The resulting coated paper was white in color, had a background O.D. of 0.02-0.06 and was resistant to marking by vigorous rubbing with a fingernail. It was shown to have a total coating weight of 4.9-6.5 g/m² and a moisture content of 6-8% by weight. The coated surface of this paper was shown to have a smoothness of 18-25 Sheffield units as measured according to TAPPI Testing Method T538 om-88, Vol. 1, 1991. It produced black images with an absorbance of 1.4-1.7 O.D. units when printed on a thermal printer.

Claims

1. A thermosensitive recording element comprising:

- (a) a support having a Sheffield smoothness of less than 60; and
- (b) at least one layer in contact with the support, said layer comprising an organic polymeric binder, a substantially colorless electron donating dye precursor and an electron accepting compound capable of forming color by reacting with said dye precursor, wherein the dye precursor and the electron accepting compound have a particle size of less than 3 µm.

2. A thermosensitive recording element comprising:

- (a) a support having a Sheffield smoothness of less than 60;

(b) a first layer comprising an organic polymeric binder and either a substantially colorless electron donating dye precursor, an electron accepting compound, or mixtures thereof; and

(c) a second layer comprising an organic polymeric binder compatible with the binder in (b) and either a substantially colorless electron donating dye precursor or an electron accepting compound, wherein both dye precursor and electron accepting compound are present in the element, wherein the first layer is interposed between the support and second layer, and wherein the dye precursor and electron accepting compound have a particle size of less than 3 μm .

3. A thermosensitive recording element comprising:

(a) a support having a Sheffield smoothness of less than 60;

(b) a first layer comprising an organic polymeric binder and a substantially colorless electron donating dye precursor; and

(c) a second layer comprising an organic polymeric binder compatible with the binder in (b), an electron accepting compound capable of forming color by reaction with said dye precursor, and a crosslinking agent, wherein the first layer is interposed between the support and the second layer, and wherein the dye precursor and the electron accepting compound have a particle size of less than 3 μm .

4. The thermosensitive recording element of claim 1, 2, or 3 wherein the support has a Sheffield smoothness of 15-25.

5. The thermosensitive recording element of claim 1, 2, or 3 wherein the support is a sheet-formed material.

6. The thermosensitive recording element of claim 5 wherein the support is paper.

7. The thermosensitive recording element of claim 6 wherein the support is selected from the group consisting 100% bleached Kraft composed of a blend of hard and soft wood, 100% wood free cotton vellum, and translucent wood-containing paper.

8. The thermosensitive recording element of claim 5 or 6 wherein the support is provided with a sealant layer.

9. The thermosensitive recording element of claim 8 wherein the sealant layer comprises an inorganic pigment and a latex sealant.

10. The thermosensitive recording element of claim 1, 2, or 3 wherein the dye precursor, and the electron accepting compound have a particle size of 0.8-1 μm .

11. The thermosensitive recording element of claim 1, 2, or 3 wherein the substantially colorless electron donating dye precursor is selected from the group consisting of triarylmethane compounds, diphenylmethane compounds, xanthene compounds, thiazine compounds and spiro compounds.

12. The thermosensitive recording element of claim 11 wherein the substantially colorless electron donating dye precursor is 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide.

13. The thermosensitive recording element of claim 11 wherein the substantially colorless electron donating dye precursor is 3-(N-ethyl-N-isopentyl)amino-6-methyl-7-anilino-fluoran.

14. The thermosensitive recording element of claim 11 wherein the substantially colorless electron donating dye precursor is 3-dipentyl-amino-6-methyl-7-aminofluoran.

15. The thermosensitive recording element of claim 1, 2, or 3 wherein the substantially colorless electron donating dye precursor is present in the amount of 1 to 15% based on the weight of the coating composition.

16. The thermosensitive recording element of claim 15 wherein the substantially colorless electron donating dye precursor is present in the amount of 3 to 8% by weight based on the weight of the coating composition.

17. The thermosensitive recording element of claim 1, 2, or 3 wherein the electron accepting compound is selected from the group consisting of phenol derivatives, aromatic carboxylic acid derivatives, N,N'-diarylthiourea derivatives, and polyvalent metal salts.

18. The thermosensitive recording element of claim 17 wherein the electron accepting compound is 2,2-bis(4'-hydroxyphenyl)propane.
19. The thermosensitive recording element of claim 17 wherein the electron accepting compound is benzyl p-hydroxybenzoate.
20. The thermosensitive recording element of claim 17 wherein the electron accepting compound is 2,2'-diallyl-4,4'-dihydroxydiphenylsulfone.
21. The thermosensitive recording element of claim 1, 2, or 3 wherein the electron accepting compound is present in the amount of 50 to 500% by weight based on the weight of the dye precursor.
22. The thermosensitive recording element of claim 21 wherein the electron accepting compound is present in the amount of 100 to 200%, by weight based on the weight of the dye precursor.
23. The thermosensitive recording element of claim 3 wherein the crosslinking agent is selected from the group consisting of mono- and polyfunctional aldehydes, blocked dialdehydes, α -diketones, active esters, active halogen compounds, s-triazines, diazines, epoxides, aziridines, halogen-substituted aldehyde acids, vinyl sulfones containing other hardening functional groups, and polymeric crosslinking agents.
24. The thermosensitive recording element of claim 23 wherein the crosslinking agent is glyoxal.
25. The thermosensitive recording element of claim 23 wherein the crosslinking agent is present in the amount of 2 to 6% based on the total layer composition.
26. The thermosensitive recording element of claim 25 wherein the crosslinking agent is present in the amount of 3 to 5% based on the total layer composition.
27. The thermosensitive recording element of claim 3 which further comprises a catalyst.
28. The thermosensitive recording element of claim 1, 2, or 3 wherein the organic polymeric binder is a water soluble binder.
29. The thermosensitive recording element of claim 28 wherein the organic polymeric binder has a molecular weight of 20,000 to 200,000.
30. The thermosensitive recording element of claim 1, 2, or 3 wherein the organic polymeric binder is selected from the group consisting of starches, hydroxyethyl cellulose, methyl cellulose, carboxymethyl cellulose, soluble collagen, gelatin, casein, polyacrylamide, polyvinyl pyrrolidone, polyvinyl alcohol, polyvinyl alcohol copolymers, sodium alginate, water soluble phenol formaldehyde resins, styrene-maleic anhydride copolymer, ethylene-maleic anhydride copolymer, ethylene vinyl acetate polymers, styrene-butadiene copolymer, acrylonitrile-butadiene copolymer, methyl acrylate-butadiene copolymer and acrylic resins.
31. The thermosensitive recording element of claim 1, 2, or 3 wherein the organic polymeric binder is obtained from an aqueous solution having a concentration of 1 to 20% by weight.
32. The thermosensitive recording element of claim 31 wherein the organic polymeric binder is obtained from an aqueous solution having a concentration of 3 to 10% by weight.
33. The thermosensitive recording element of claim 1 or 2 wherein at least one additional layer is present.
34. The thermosensitive recording element of claim 33 wherein the additional layer is the outermost layer and comprises an organic polymeric binder and either a dye precursor or an electron accepting compound.
35. The thermosensitive recording element of claim 3 wherein at least one additional layer is present.
36. The thermosensitive recording element of claim 35 wherein the additional layer is the outermost layer and comprises an organic polymeric binder, an electron accepting compound and a crosslinking agent.

37. A process for preparing a thermosensitive recording element comprising the steps of:

- (a) providing a support;
- (b) preparing a first dispersion of an aqueous solution comprising an organic polymeric binder and a substantially colorless, electron donating dye precursor;
- (c) preparing a second dispersion of an aqueous solution comprising an organic polymeric binder, an electron accepting compound capable of forming color by reaction with said dye precursor, wherein the binder is compatible with the binder in (b);
- (d) preparing a mixture of the first and second dispersions;
- (e) applying the mixture of the first and second dispersions onto the support;
- (f) drying the dispersion applied in step (e) to form a first layer on the support, wherein the support has a Sheffield smoothness of less than 60, and the dye precursor and the electron accepting compound have a particle size of less than 3 μm .

38. A process for preparing a thermosensitive recording element comprising the steps of:

- (a) providing a support;
- (b) preparing a first dispersion of an aqueous solution of an organic polymeric binder containing a substantially colorless, electron donating dye precursor;
- (c) preparing a second dispersion of an aqueous solution of an organic polymeric binder containing an electron accepting compound, wherein the binder is compatible with the binder in (b);
- (d) applying either the first dispersion, the second dispersion or a mixture thereof onto the support;
- (e) drying the first applied dispersion to form a first layer on the support;
- (f) applying either the first dispersion or the second dispersion on the first layer formed in step (e); and
- (g) drying the dispersion applied in step (f) to form a thermosensitive recording element having a support bearing at least two layers, wherein the support has a Sheffield smoothness of less than 60, and the dye precursor, and electron accepting compound have a particle size of less than 3 μm .

39. A process for preparing a thermosensitive recording element having a support bearing at least two layers comprising the steps of:

- (a) providing a support;
- (b) preparing a first dispersion of an aqueous solution comprising an organic polymeric binder and a substantially colorless, electron donating dye precursor;
- (c) preparing a second dispersion of an aqueous solution comprising an organic polymeric binder compatible with the binder in (b), an electron accepting compound capable of forming color by reaction with said dye precursor, and a crosslinking agent;
- (d) applying the first dispersion onto the support;
- (e) drying the applied first dispersion to form a first layer formed in step (e);
- (f) applying the second dispersion on the first layer on the support; and
- (g) drying the second applied dispersion to form a second layer, wherein the support has a Sheffield smoothness of less than 60, and the dye precursor and the electron accepting compound have a particle size of less than 3 μm .

40. The process of claim 37, 38, or 39 wherein the dye precursor and electron accepting compound each have a particle size of 0.5 to 3 μm .

41. The process of claim 40 wherein the dye precursor and electron accepting compound each have a particle size of 0.8 to 1 μm .

42. The process of claim 38 or 39 wherein at least one additional dispersion is applied to the thermosensitive recording element after step (g).

43. The process of claim 42 wherein the applied dispersion is dried to form a thermosensitive recording element having a support bearing at least three layers.

44. The process of claim 37, 38, or 39 wherein the support has a Sheffield smoothness of 15-25.

Patentansprüche

1. Wärmeempfindliches Aufzeichnungselement, umfassend:

- (a) einen Träger mit einer Sheffield-Glätte von weniger als 60; und
 (b) wenigstens eine Schicht in Kontakt mit dem Träger, wobei die Schicht ein organisches polymeres Bindemittel, eine im wesentlichen farblose elektronenabgebende Farbstoffvorstufe und eine elektronenaufnehmende Verbindung, die durch Reaktion mit der Farbstoffvorstufe eine Farbe bilden kann, umfaßt, wobei die Farbstoffvorstufe und die elektronenaufnehmende Verbindung eine Teilchengröße von weniger als 3 µm haben.

2. Wärmeempfindliches Aufzeichnungselement, umfassend:

- (a) einen Träger mit einer Sheffield-Glätte von weniger als 60;
 (b) eine erste Schicht, die ein organisches polymeres Bindemittel und entweder eine im wesentlichen farblose elektronenabgebende Farbstoffvorstufe, eine elektronenaufnehmende Verbindung oder Gemische davon umfaßt; und
 (c) eine zweite Schicht, die ein organisches polymeres Bindemittel, das mit dem Bindemittel in (b) verträglich ist, und entweder eine im wesentlichen farblose elektronenabgebende Farbstoffvorstufe oder eine elektronenaufnehmende Verbindung umfaßt, wobei sowohl die Farbstoffvorstufe als auch die elektronenaufnehmende Verbindung in dem Element vorhanden sind, wobei sich die erste Schicht zwischen dem Träger und der zweiten Schicht befindet und wobei die Farbstoffvorstufe und die elektronenaufnehmende Verbindung eine Teilchengröße von weniger als 3 µm haben.

3. Wärmeempfindliches Aufzeichnungselement, umfassend:

- (a) einen Träger mit einer Sheffield-Glätte von weniger als 60;
 (b) eine erste Schicht, die ein organisches polymeres Bindemittel und eine im wesentlichen farblose elektronenabgebende Farbstoffvorstufe umfaßt; und
 (c) eine zweite Schicht, die ein organisches polymeres Bindemittel, das mit dem Bindemittel in (b) verträglich ist, eine elektronenaufnehmende Verbindung, die durch Reaktion mit der Farbstoffvorstufe eine Farbe bilden kann, sowie ein Vernetzungsmittel umfaßt, wobei sich die erste Schicht zwischen dem Träger und der zweiten Schicht befindet und wobei die Farbstoffvorstufe und die elektronenaufnehmende Verbindung eine Teilchengröße von weniger als 3 µm haben.

4. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 1, 2 oder 3, wobei der Träger eine Sheffield-Glätte von 15-25 hat.

5. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 1, 2 oder 3, wobei der Träger aus einem blattförmigen Material besteht.

6. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 5, wobei der Träger aus Papier besteht.

7. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 6, wobei der Träger aus der Gruppe ausgewählt ist, die aus 100% gebleichtem Kraftpapier, das aus einem Gemisch von Hart- und Weichholz zusammengesetzt ist, 100% holzfreiem Baumwollpergamentpapier und durchscheinendem holzhaltigem Papier besteht.

8. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 5 oder 6, wobei der Träger mit einer Versiegelungsschicht ausgestattet ist.

9. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 8, wobei die Versiegelungsschicht ein anorganisches Pigment und ein Latexversiegelungsmittel umfaßt.

10. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 1, 2 oder 3, wobei die Farbstoffvorstufe und die elektronenaufnehmende Verbindung eine Teilchengröße von 0,8-1 µm haben.

11. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 1, 2 oder 3, wobei die im wesentlichen farblose elektronenabgebende Farbstoffvorstufe aus der Gruppe ausgewählt ist, die aus Triarylmethanverbindungen, Diphenylmethanverbindungen, Xanthenverbindungen, Thiazinverbindungen und Spiroverbindungen besteht.

12. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 11, wobei es sich bei der im wesentlichen farblosen elektronenabgebenden Farbstoffvorstufe um 3,3-Bis(p-dimethylaminophenyl)-6-dimethylaminophthalid handelt.
- 5 13. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 11, wobei es sich bei der im wesentlichen farblosen elektronenabgebenden Farbstoffvorstufe um 3-(N-Ethyl-N-isopentyl)-amino-6-methyl-7-anilino-fluoran handelt.
14. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 11, wobei es sich bei der im wesentlichen farblosen elektronenabgebenden Farbstoffvorstufe um 3-Dipentylamino-6-methyl-7-anilino-fluoran handelt.
- 10 15. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 1, 2 oder 3, wobei die im wesentlichen farblose elektronenabgebende Farbstoffvorstufe in einer Menge von 1 bis 15%, bezogen auf das Gewicht der Beschichtungszusammensetzung, vorhanden ist.
- 15 16. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 15, wobei die im wesentlichen farblose elektronenabgebende Farbstoffvorstufe in einer Menge von 3 bis 8%, bezogen auf das Gewicht der Beschichtungszusammensetzung, vorhanden ist.
- 20 17. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 1, 2 oder 3, wobei die elektronenaufnehmende Verbindung aus der Gruppe ausgewählt ist, die aus Phenolderivaten, Derivaten aromatischer Carbonsäuren, N,N'-Diarylthioharnstoffderivaten und Salzen mehrwertiger Metalle besteht.
18. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 17, wobei es sich bei der elektronenaufnehmenden Verbindung um 2,2-Bis(4'-hydroxyphenyl)propan handelt.
- 25 19. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 17, wobei es sich bei der elektronenaufnehmenden Verbindung um Benzyl-p-hydroxybenzoat handelt.
20. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 17, wobei es sich bei der elektronenaufnehmenden Verbindung um 2,2'-Diallyl-4,4'-dihydroxydiphenylsulfon handelt.
- 30 21. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 1, 2 oder 3, wobei die elektronenaufnehmende Verbindung in einer Menge von 50 bis 500 Gew.-%, bezogen auf das Gewicht der Farbstoffvorstufe, vorhanden ist.
- 35 22. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 21, wobei die elektronenaufnehmende Verbindung in einer Menge von 100 bis 200 Gew.-%, bezogen auf das Gewicht der Farbstoffvorstufe, vorhanden ist.
- 40 23. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 3, wobei das Vernetzungsmittel aus der Gruppe ausgewählt ist, die aus mono- und polyfunktionellen Aldehyden, blockierten Dialdehyden, α -Diketonen, aktiven Estern, aktiven Halogenverbindungen, s-Triazinen, Diazinen, Epoxiden, Aziridinen, halogensubstituierten Aldehydsäuren, Vinylsulfonen, die andere härtende funktionelle Gruppen enthalten, und polymeren Vernetzungsmitteln besteht.
24. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 23, wobei es sich bei dem Vernetzungsmittel um Glyoxal handelt.
- 45 25. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 23, wobei das Vernetzungsmittel in einer Menge von 2 bis 6%, bezogen auf die Gesamtschichtzusammensetzung, vorhanden ist.
26. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 25, wobei das Vernetzungsmittel in einer Menge von 3 bis 5%, bezogen auf die Gesamtschichtzusammensetzung, vorhanden ist.
- 50 27. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 3, das weiterhin einen Katalysator umfaßt.
28. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 1, 2 oder 3, wobei das organische polymere Bindemittel ein wasserlösliches Bindemittel ist.
- 55 29. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 28, wobei das organische polymere Bindemittel ein Molekulargewicht von 20000 bis 200000 hat.

- 5 30. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 1, 2 oder 3, wobei das organische polymere Bindemittel aus der Gruppe ausgewählt ist, die aus Stärken, Hydroxyethylcellulose, Methylcellulose, Carboxymethylcellulose, löslichem Collagen, Gelatine, Casein, Polyacrylamid, Polyvinylpyrrolidon, Polyvinylalkohol, Polyvinylalkohol-Copolymere, Natriumalginat, wasserlöslichen Phenol-Formaldehyd-Harzen, Styrol/Maleinsäureanhydrid-Copolymer, Ethylen/Maleinsäureanhydrid-Copolymer, Ethylen/Vinylacetat-Polymeren, Styrol/Butadien-Copolymer, Acrylnitril/Butadien-Copolymer, Methylacrylat/Butadien-Copolymer und Acrylharzen besteht.
- 10 31. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 1, 2 oder 3, wobei das organische polymere Bindemittel aus einer wäßrigen Lösung mit einer Konzentration von 1 bis 20 Gew.-% erhalten wird.
- 15 32. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 31, wobei das organische polymere Bindemittel aus einer wäßrigen Lösung mit einer Konzentration von 3 bis 10 Gew.-% erhalten wird.
- 20 33. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 1 oder 2, wobei wenigstens eine zusätzliche Schicht vorhanden ist.
- 25 34. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 33, wobei die zusätzliche Schicht die äußerste Schicht ist und ein organisches polymeres Bindemittel sowie entweder eine Farbstoffvorstufe oder eine elektronenaufnehmende Verbindung umfaßt.
- 30 35. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 3, wobei wenigstens eine zusätzliche Schicht vorhanden ist.
- 35 36. Wärmeempfindliches Aufzeichnungselement gemäß Anspruch 35, wobei die zusätzliche Schicht die äußerste Schicht ist und ein organisches polymeres Bindemittel, eine elektronenaufnehmende Verbindung und ein Vernetzungsmittel umfaßt.
- 40 37. Verfahren zur Herstellung eines wärmeempfindlichen Aufzeichnungselements, umfassend die Schritte:
- (a) Bereitstellen eines Trägers;
- (b) Herstellen einer ersten Dispersion einer wäßrigen Lösung, die ein organisches polymeres Bindemittel und eine im wesentlichen farblose elektronenabgebende Farbstoffvorstufe umfaßt;
- (c) Herstellen einer zweiten Dispersion einer wäßrigen Lösung, die ein organisches polymeres Bindemittel, eine elektronenaufnehmende Verbindung, die durch Reaktion mit der Farbstoffvorstufe eine Farbe bilden kann, umfaßt, wobei das Bindemittel mit dem Bindemittel in (b) verträglich ist;
- (d) Herstellen eines Gemischs aus der ersten und der zweiten Dispersion;
- (e) Auftragen des Gemischs aus der ersten und der zweiten Dispersion auf den Träger;
- (f) Trocknen der in Schritt (e) aufgetragenen Dispersion unter Bildung einer ersten Schicht auf dem Träger,
- wobei der Träger eine Sheffield-Glätte von weniger als 60 hat und die Farbstoffvorstufe und die elektronenaufnehmende Verbindung eine Teilchengröße von weniger als 3 µm haben.
- 45 38. Verfahren zur Herstellung eines wärmeempfindlichen Aufzeichnungselements, umfassend die Schritte:
- (a) Bereitstellen eines Trägers;
- (b) Herstellen einer ersten Dispersion einer wäßrigen Lösung eines organischen polymeren Bindemittels, die eine im wesentlichen farblose elektronenabgebende Farbstoffvorstufe enthält;
- (c) Herstellen einer zweiten Dispersion einer wäßrigen Lösung eines organischen polymeren Bindemittels, die eine elektronenaufnehmende Verbindung enthält, wobei das Bindemittel mit dem Bindemittel in (b) verträglich ist;
- (d) Auftragen entweder der ersten Dispersion, der zweiten Dispersion oder eines Gemisches davon auf den Träger;
- (e) Trocknen der ersten aufgetragenen Dispersion unter Bildung einer ersten Schicht auf dem Träger;
- (f) Auftragen entweder der ersten Dispersion oder der zweiten Dispersion auf die in Schritt (e) gebildete erste Schicht; und
- (g) Trocknen der in Schritt (f) aufgetragenen Dispersion unter Bildung eines wärmeempfindlichen Aufzeichnungselements mit einem Träger, der wenigstens zwei Schichten trägt,

wobei der Träger eine Sheffield-Glätte von weniger als 60 hat und die Farbstoffvorstufe und die elektronenaufnehmende Verbindung eine Teilchengröße von weniger als 3 µm haben.

39. Verfahren zur Herstellung eines wärmeempfindlichen Aufzeichnungselements mit einem Träger, der wenigstens zwei Schichten trägt, umfassend die Schritte:

- (a) Bereitstellen eines Trägers;
- (b) Herstellen einer ersten Dispersion einer wäßrigen Lösung, die ein organisches polymeres Bindemittel und eine im wesentlichen farblose elektronenabgebende Farbstoffvorstufe umfaßt;
- (c) Herstellen einer zweiten Dispersion einer wäßrigen Lösung, die ein organisches polymeres Bindemittel, das mit dem Bindemittel in (b) verträglich ist, eine elektronenaufnehmende Verbindung, die durch Reaktion mit der Farbstoffvorstufe eine Farbe bilden kann, und ein Vernetzungsmittel umfaßt;
- (d) Auftragen der ersten Dispersion auf den Träger;
- (e) Trocknen der aufgetragenen ersten Dispersion unter Bildung einer in Schritt (e) gebildeten ersten Schicht;
- (f) Auftragen der zweiten Dispersion auf die erste Schicht auf dem Träger; und
- (g) Trocknen der zweiten aufgetragenen Dispersion unter Bildung einer zweiten Schicht,

wobei der Träger eine Sheffield-Glätte von weniger als 60 hat und die Farbstoffvorstufe und die elektronenaufnehmende Verbindung eine Teilchengröße von weniger als 3 µm haben.

40. Verfahren gemäß Anspruch 37, 38 oder 39, wobei die Farbstoffvorstufe und die elektronenaufnehmende Verbindung jeweils eine Teilchengröße von 0,5 bis 3 µm haben.

41. Verfahren gemäß Anspruch 40, wobei die Farbstoffvorstufe und die elektronenaufnehmende Verbindung jeweils eine Teilchengröße von 0,8 bis 1 µm haben.

42. Verfahren gemäß Anspruch 38 oder 39, wobei nach Schritt (g) wenigstens eine weitere Dispersion auf das wärmeempfindliche Aufzeichnungselement aufgetragen wird.

43. Verfahren gemäß Anspruch 42, wobei die aufgetragene Dispersion unter Bildung eines wärmeempfindlichen Aufzeichnungselements mit einem Träger, der wenigstens drei Schichten trägt, getrocknet wird.

44. Verfahren gemäß Anspruch 37, 38 oder 39, wobei der Träger eine Sheffield-Glätte von 15-25 hat.

Revendications

1. Élément d'enregistrement thermosensible comprenant :

- (a) un support ayant un lissé Sheffield inférieur à 60, et
- (b) au moins une couche en contact avec le support, ladite couche comprenant un liant polymère organique, un précurseur de colorant donneur d'électrons sensiblement incolore et un composé receveur d'électrons susceptible de former une couleur par réaction avec ledit précurseur de colorant, élément dans lequel le précurseur de colorant et le composé receveur d'électrons ont une taille particulière inférieure à 3 µm.

2. Élément d'enregistrement thermosensible comprenant :

- (a) un support ayant un lissé Sheffield inférieur à 60,
- (b) une première couche comprenant un liant polymère organique et un précurseur de colorant donneur d'électrons sensiblement incolore ou un composé receveur d'électrons, ou leurs mélanges, et
- (c) une deuxième couche comprenant un liant polymère organique compatible avec le liant de (b) et un précurseur de colorant donneur d'électrons sensiblement incolore ou un composé receveur d'électrons, élément dans lequel à la fois le précurseur de colorant et le composé receveur d'électrons sont présents dans l'élément, la première couche est intercalée entre le support et la deuxième couche, et le précurseur de colorant et le composé receveur d'électrons ont une taille particulière inférieure à 3 µm.

3. Élément d'enregistrement thermosensible comprenant :

- (a) un support ayant un lissé Sheffield inférieur à 60,

(b) une première couche comprenant un liant polymère organique et un précurseur de colorant donneur d'électrons sensiblement incolore, et

(c) une deuxième couche comprenant un liant polymère organique compatible avec le liant de (b), un composé receveur d'électrons susceptible de former une couleur par réaction avec ledit précurseur de colorant, et un agent de réticulation, élément dans lequel la première couche est intercalée entre le support et la deuxième couche, et le précurseur de colorant et le composé receveur d'électrons ont une taille particulière inférieure à 3 μm .

4. Élément d'enregistrement thermosensible selon la revendication 1, 2 ou 3, dans lequel le support a un lissé Sheffield de 15 à 25.

5. Élément d'enregistrement thermosensible selon la revendication 1, 2 ou 3, dans lequel le support est une matière en forme de feuille.

6. Élément d'enregistrement thermosensible selon la revendication 5, dans lequel le support est du papier.

7. Élément d'enregistrement thermosensible selon la revendication 6, dans lequel le support est choisi dans le groupe comprenant du papier Kraft 100 % blanchi composé d'un mélange de fibres de feuillus et de résineux, un velin de coton 100 % sans bois et un papier translucide avec bois.

8. Élément d'enregistrement thermosensible selon la revendication 5 ou 6, dans lequel le support est pourvu d'une couche d'un agent d'étanchéité.

9. Élément d'enregistrement thermosensible selon la revendication 8, dans lequel la couche d'agent d'étanchéité comprend un pigment minéral et un agent d'étanchéité de type latex.

10. Élément d'enregistrement thermosensible selon la revendication 1, 2 ou 3, dans lequel le précurseur de colorant et le composé receveur d'électrons ont une taille particulière de 0,8 à 1 μm .

11. Élément d'enregistrement thermosensible selon la revendication 1, 2 ou 3, dans lequel le précurseur de colorant donneur d'électrons sensiblement incolore est sélectionné dans le groupe comprenant des composés de triarylméthane, des composés de diphenylméthane, des composés de xanthène, des composés de thiazine et des composés spiro.

12. Élément d'enregistrement thermosensible selon la revendication 11, dans lequel le précurseur de colorant donneur d'électrons sensiblement incolore est le 3,3-bis(p-diméthylaminophényl)-6-diméthylaminophthalide.

13. Élément d'enregistrement thermosensible selon la revendication 11, dans lequel le précurseur de colorant donneur d'électrons sensiblement incolore est le 3-(N-éthyl-N-isopentyl)-amino-6-méthyl-7-anilino-fluoranne.

14. Élément d'enregistrement thermosensible selon la revendication 11, dans lequel le précurseur de colorant donneur d'électrons sensiblement incolore est le 3-dipentyl-amino-6-méthyl-7-aminofluoranne.

15. Élément d'enregistrement thermosensible selon la revendication 1, 2 ou 3, dans lequel le précurseur de colorant donneur d'électrons sensiblement incolore est présent en quantité de 1 à 15 % en poids sur la base du poids de la composition de revêtement.

16. Élément d'enregistrement thermosensible selon la revendication 15, dans lequel le précurseur de colorant donneur d'électrons sensiblement incolore est présent en quantité de 3 à 8 % en poids sur la base du poids de la composition de revêtement.

17. Élément d'enregistrement thermosensible selon la revendication 1, 2 ou 3, dans lequel le composé receveur d'électrons est sélectionné dans le groupe comprenant des dérivés de phénol, des dérivés d'acides carboxyliques aromatiques, des dérivés de N,N'-diaryliourée et des sels métalliques polyvalents.

18. Élément d'enregistrement thermosensible selon la revendication 17, dans lequel le composé receveur d'électrons est le 2,2-bis(4'-hydroxyphényl)propane.

19. Elément d'enregistrement thermosensible selon la revendication 17, dans lequel le composé receveur d'électrons est le p-hydroxybenzoate de benzyle.
- 5 20. Elément d'enregistrement thermosensible selon la revendication 17, dans lequel le composé receveur d'électrons est la 2,2'-diallyl-4,4'-dihydroxydiphénylsulfone.
21. Elément d'enregistrement thermosensible selon la revendication 1, 2 ou 3, dans lequel le composé receveur d'électrons est présent en quantité de 50 à 500 % en poids sur la base du poids du précurseur de colorant.
- 10 22. Elément d'enregistrement thermosensible selon la revendication 21, dans lequel le composé receveur d'électrons est présent en quantité de 100 à 200 % en poids sur la base du poids du précurseur de colorant.
- 15 23. Elément d'enregistrement thermosensible selon la revendication 3, dans lequel l'agent de réticulation est sélectionné dans le groupe comprenant des aldéhydes mono- et polyfonctionnels, des dialdéhydes bloqués, des α -dicétones, des esters actifs, des composés halogénés actifs, des s-triazines, des diazines, des époxydes, des aziridines, des acides aldéhydes substitués par des halogènes, des vinyl sulfones contenant d'autres groupes fonctionnels durcisants, et des agents de réticulation polymères.
- 20 24. Elément d'enregistrement thermosensible selon la revendication 23, dans lequel l'agent de réticulation est le glyoxal.
- 25 25. Elément d'enregistrement thermosensible selon la revendication 23, dans lequel l'agent de réticulation est présent en quantité de 2 à 6 % sur la base de la composition totale de la couche.
- 26 26. Elément d'enregistrement thermosensible selon la revendication 25, dans lequel l'agent de réticulation est présent en quantité de 3 à 5 % sur la base de la composition totale de la couche.
27. Elément d'enregistrement thermosensible selon la revendication 3, qui comprend par ailleurs un catalyseur.
- 30 28. Elément d'enregistrement thermosensible selon la revendication 1, 2 ou 3, dans lequel le liant polymère organique est un liant soluble dans l'eau.
- 35 29. Elément d'enregistrement thermosensible selon la revendication 28, dans lequel le liant polymère organique a un poids moléculaire de 20.000 à 200.000.
- 40 30. Elément d'enregistrement thermosensible selon la revendication 1, 2 ou 3, dans lequel le liant polymère organique est sélectionné dans le groupe comprenant des amidons, l'hydroxyéthyl cellulose, la méthyl cellulose, la carboxyméthyl cellulose, le collagène soluble, la gélatine, la caséine, le polyacrylamide, la polyvinyl pyrrolidone, l'alcool polyvinylique, des copolymères d'alcool polyvinylique, l'alginate de sodium, des résines de phénol formaldéhyde solubles dans l'eau, un copolymère de styrène et d'anhydride maléique, un copolymère d'éthylène et d'anhydride maléique, des polymères d'éthylène et d'acétate de vinyle, un copolymère de styrène et de butadiène, un copolymère d'acrylonitrile et de butadiène, un copolymère d'acrylate de méthyle et de butadiène et des résines acryliques.
- 45 31. Elément d'enregistrement thermosensible selon la revendication 1, 2 ou 3, dans lequel le liant polymère organique est obtenu à partir d'une solution aqueuse ayant une concentration de 1 à 20% en poids.
- 50 32. Elément d'enregistrement thermosensible selon la revendication 31, dans lequel le liant polymère organique est obtenu à partir d'une solution aqueuse ayant une concentration de 3 à 10 % en poids.
- 55 33. Elément d'enregistrement thermosensible selon la revendication 1 ou 2, dans lequel au moins une couche supplémentaire est présente.
34. Elément d'enregistrement thermosensible selon la revendication 33, dans lequel la couche supplémentaire est la couche externe et comprend un liant polymère organique et un précurseur de colorant ou un composé receveur d'électrons.
35. Elément d'enregistrement thermosensible selon la revendication 3, dans lequel au moins une couche supplémentaire est présente.

36. Elément d'enregistrement thermosensible selon la revendication 35, dans lequel la couche supplémentaire est la couche externe et comprend un liant polymère organique, un composé receveur d'électrons et un agent de réticulation.

5 37. Procédé de préparation d'un élément d'enregistrement thermosensible comprenant les stades suivants :

(a) on met en oeuvre un support,

(b) on prépare une première dispersion d'une solution aqueuse comprenant un liant polymère organique et un précurseur de colorant donneur d'électrons sensiblement incolore,

10 (c) on prépare une deuxième dispersion d'une solution aqueuse comprenant un liant polymère organique, un composé receveur d'électrons susceptible de former une couleur par réaction avec ledit précurseur de colorant, procédé dans lequel le liant est compatible avec le liant de (b),

(d) on prépare un mélange de la première et de la deuxième dispersions,

(e) on applique le mélange de la première et de la deuxième dispersions sur le support,

15 (f) on sèche la dispersion appliquée au stade (e) pour former une première couche sur le support, le support ayant un lissé Sheffield inférieur à 60, et le précurseur de colorant et le composé receveur d'électrons ayant une taille particulaire inférieure à 3 μm .

38. Procédé de préparation d'un élément d'enregistrement thermosensible comprenant les stades suivants :

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(a) on met en oeuvre un support,

(b) on prépare une première dispersion d'une solution aqueuse d'un liant polymère organique contenant un précurseur de colorant donneur d'électrons sensiblement incolore,

25 (c) on prépare une deuxième dispersion d'une solution aqueuse d'un liant polymère organique contenant un composé receveur d'électrons, le liant étant compatible avec le liant de (b),

(d) on applique la première dispersion ou la deuxième dispersion ou un mélange de celles-ci sur le support,

(e) on sèche la première dispersion appliquée pour former une première couche sur le support,

(f) on applique la première dispersion ou la deuxième dispersion sur la première couche formée au stade (e), et

30 (g) on sèche la dispersion appliquée au stade (f) pour former un élément d'enregistrement thermosensible ayant un support portant au moins deux couches, le support ayant un lissé Sheffield inférieur à 60, et le précurseur de colorant et le composé receveur d'électrons ayant une taille particulaire inférieure à 3 μm .

39. Procédé de préparation d'un élément d'enregistrement thermosensible ayant un support portant au moins deux couches, comprenant les stades suivants :

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(a) on met en oeuvre un support,

(b) on prépare une première dispersion d'une solution aqueuse comprenant un liant polymère organique et un précurseur de colorant donneur d'électrons sensiblement incolore,

40 (c) on prépare une deuxième dispersion d'une solution aqueuse comprenant un liant polymère organique compatible avec le liant de (b), un composé receveur d'électrons susceptible de former une couleur par réaction avec ledit précurseur de colorant, et un agent de réticulation,

(d) on applique la première dispersion sur le support,

(e) on sèche la première dispersion appliquée pour former une première couche formée au stade (e),

(f) on applique la deuxième dispersion sur la première couche sur le support, et

45 (g) on sèche la deuxième dispersion appliquée pour former une deuxième couche, le support ayant un lissé Sheffield inférieur à 60, et le précurseur de colorant et le composé receveur d'électrons ayant une taille particulaire inférieure à 3 μm .

50 40. Procédé selon la revendication 37, 38 ou 39, dans lequel le précurseur de colorant et le composé receveur d'électrons ont chacun une taille particulaire de 0,5 à 3 μm .

41. Procédé selon la revendication 40, dans lequel le précurseur de colorant et le composé receveur d'électrons ont chacun une taille particulaire de 0,8 à 1 μm .

55 42. Procédé selon la revendication 38 ou 39, dans lequel au moins une dispersion supplémentaire est appliquée à l'élément d'enregistrement thermosensible après le stade (g).

43. Procédé selon la revendication 42, dans lequel la dispersion appliquée est séchée pour former un élément d'enregistrement thermosensible ayant un support portant au moins trois couches.

44. Procédé selon la revendication 37, 38 ou 39, dans lequel le support a un lissé Sheffield de 15 à 25.

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